A Prototype Engineering Equation of State for Solids

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We commonly use equations of state in chemical engineering to estimate the thermodynamic properties for fluids. By contrast, we commonly use empirical correlations to estimate the thermodynamic properties for solids. Such empirical correlations, for example for density, heat capacity, and melting pressure, are not very predictive and require extensive experimental data. We have little choice, however, because there is no equation of state available for solids yet. Our general goal, therefore, is to develop predictive thermodynamic models for complex solids. Our immediate goal is to develop an equation of state (EOS) on the basis of the modified Weeks-Chandler-Andersen (WCA) perturbation theory for Lennard-Jones-like solids. This is now possible as a result of new developments in the theory of hard-sphere solids, which led to an accurate equation of state and radial distribution function (rdf); these are needed as the reference for the WCA perturbation theory. We test this approach on real "single-segment" molecules, such as argon, krypton, and methane for which we have accurate experimental data. We find that this EOS accurately predicts the melting pressure and molar solid volume of these systems, which has not been demonstrated to date. The next challenge is to extend this approach to more complex real systems, such as polymers.